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Mechanisms of changes of hole concentration in Al-doped 6H-SiC by electron irradiation and annealing

Hideharu Matsuura ^{a,*}, Hideki Yanagisawa ^a, Kozo Nishino ^a, Yoshiko Myojin ^a, Takunori Nojiri ^a, Yukei Matsuyama ^a, Takeshi Ohshima ^b

^a Osaka Electro-Communication University, 18-8 Hatsu-cho, Neyagawa, Osaka 572-8530, Japan ^b Japan Atomic Energy Agency, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan

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ABSTRACT

The temperature dependence of the hole concentration p(T) in Al-doped p-type 6H-SiC irradiated by 100 or 200 keV electrons is investigated. Since p(T) is unchanged by 100 keV electron irradiation, the threshold displacement energy in SiC is higher than 20 eV. Therefore, 200 keV electrons cannot displace substitutional Si and Al in Al-doped 6H-SiC. Using p(T), two types of acceptor species are detected, and the density and energy level of each acceptor species are determined. By 200 keV electron irradiation, the density (N_{Al}) of the shallow acceptor (i.e., Al acceptor) decreases monotonously with increasing fluence of electrons, whereas the density (N_{DA}) of the deep acceptor initially increases and then decreases. By irradiation with the 1 × 10¹⁶ cm⁻² fluence of 200 keV electrons, especially, the decrement of N_{Al} is nearly equal to the increment of N_{DA} . By annealing at 500 °C, on the other hand, the increment of N_{Al} is close to the decrement of N_{DA} .

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1. Introduction

Silicon carbide (SiC) is a promising wide bandgap semiconductor for fabricating high-power and high-frequency electronic devices capable of operating at elevated temperatures under radiation environment.

By comparing electron-radiation damage in p-type 4H-SiC with that in p-type Si [1–4], it was found that the reduction in the temperature-dependent hole concentration p(T) in Al-doped p-type 4H-SiC by electron irradiation was much larger than in Al-doped p-type Si.

In the analyses of p(T) in lightly Al-doped p-type 4H-SiC epilayers, the density (N_{Al}) of Al acceptors with the energy level (E_{Al}) of $E_V + 0.22 \text{ eV}$ significantly decreased with increasing fluence (Φ) of 200 keV electrons, whereas the density (N_{DA}) of deep acceptors with the energy level (E_{DA}) of $E_V + 0.38 \text{ eV}$ initially increased with Φ and then decreased [4,5], where E_V is the valence band maximum. The reduction in p(T) by 200 keV electron irradiation was mainly due to the decrease in Al acceptors and not due to the increase in C vacancies (V_C) created by irradiation [4,5]. In unirradiated epilayers, on the other hand, the relationship of $N_{DA} = 0.6N_{Al}$ was obtained in a range of N_{Al} between 8×10^{14} and $5 \times 10^{16} \text{ cm}^{-3}$ [6,7], suggesting that the deep acceptors may be

E-mail address: matsuura@isc.osakac.ac.jp (H. Matsuura).

related to Al. From these experimental results, differential equations describing the dependence of N_{AI} and N_{DA} on Φ were proposed as [5]

$$\frac{\mathrm{d}N_{\mathrm{Al}}}{\mathrm{d}\Phi} = -\kappa_{\mathrm{Al}}N_{\mathrm{Al}} \tag{1}$$

and

$$\frac{\mathrm{d}N_{\mathrm{DA}}}{\mathrm{d}\Phi} = -\frac{\mathrm{d}N_{\mathrm{AI}}}{\mathrm{d}\Phi} - \kappa_{\mathrm{DA}}N_{\mathrm{DA}},\tag{2}$$

where κ_{Al} and κ_{DA} are the removal cross sections of Al acceptors and deep acceptors for 200 keV electron irradiation, respectively. By fitting the curve to the experimental dependence of N_{Al} or N_{DA} on Φ , the values of κ_{Al} and κ_{DA} were determined to be 4.4×10^{-17} and 1.0×10^{-17} cm², respectively [5].

From p(T) for lightly Al-doped 6H-SiC epilayers, an acceptor species with $E_V + \sim 0.2 \text{ eV}$ was observed [8,9]. From photoluminescence [10], the acceptor species is ascribed to an Al atom (Al_{si}) at a Si sublattice site. In heavily Al-implanted p-type 6H-SiC layers, the removal cross section of Al acceptors for 1 MeV electron irradiation was determined to be $6.4 \times 10^{-18} \text{ cm}^2$ [11]. Since 6H-SiC is expected to be a suitable polytype for electronic devices used in high-energy radiation environments besides 4H-SiC, we report on the reduction in p(T) in lightly Al-doped p-type 6H-SiC epilayers by 100 or 200 keV electron irradiation.





^{*} Corresponding author. Tel./fax: +81728209031.

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2. Experimental

A 4.9 µm-thick lightly Al-doped p-type 6H-SiC epilayer on ntype 6H-SiC (resistivity: 0.027Ω cm) was cut to a 1×1 cm² size. Ohmic metal (Ti/Al) was deposited on the four corners of the surface of the sample, and then the sample was annealed at 900 °C for 1 min in an Ar atmosphere. The p(T) was measured by van der Pauw configuration in the temperature range from 200 to 600 K in a magnetic field of 1.4T using a modified MMR Technologies' Hall system. After the sample was irradiated with 200 keV electrons with a fluence of 1.0×10^{16} cm⁻² at room temperature, the Halleffect measurement was carried out. The sample was again irradiated with the same fluence, and then the measurement was done. These processes were repeated. Consequently, p(T) values for total fluences (Φ) of 0, 1.0, 2.0, and $3.0 \times 10^{16} \, \mathrm{cm^{-2}}$ were measured. However, p(T) at Φ of 3.0×10^{16} cm⁻² could not be obtained. After annealing the sample at 500 °C for 2 min in an Ar atmosphere, therefore, the Hall-effect measurement was carried out. Another sample was irradiated with 100 keV electrons with Φ of 0, 1.0, 3.0, and $5.0 \times 10^{16} \text{ cm}^{-2}$, and these p(T) values were obtained.

The densities and energy levels of acceptors and hole traps were determined by free carrier concentration spectroscopy (FCCS) from p(T). Here, FCCS is a graphical peak analysis method to determine them without any assumptions regarding acceptor species or hole traps. Using p(T), the FCCS signal is defined as

$$H(T, E_{\rm ref}) \equiv \frac{p(T)^2}{(kT)^{5/2}} \exp\left(\frac{E_{\rm ref}}{kT}\right),\tag{3}$$

where *k* is the Boltzmann constant and E_{ref} is the parameter that can shift the peak temperature of the FCCS signal within the temperature range of the measurement. The FCCS signal has a peak at the temperature corresponding to each acceptor level or hole-trap level. From each peak, the density and energy level of the corresponding acceptor or hole trap can be accurately determined. The application software of FCCS for the Windows operating system can be downloaded for free at our Web site (http://www.osakac.ac.jp/labs/matsuura/).

3. Results and discussion

Fig. 1 shows the experimental p(T) before irradiation (\bigcirc) and after irradiation with 200 keV electrons with Φ of 1.0×10^{16} cm⁻² (\blacktriangle) and 2.0×10^{16} cm⁻² (\Box). Since p(T) at Φ of 3.0×10^{16} cm⁻² could not be measured, the sample was annealed at 500 °C for 2 min. The p(T) in the annealed sample is denoted by + in Fig. 1. Although the Hall-effect measurements were carried out twice for each fluence, p(T) remained unchanged, indicating that any acceptors and defects affecting p(T) were not annealed for measurement temperatures lower than 600 K, that is, 327 °C.

Using the p(T) for the unirradiated sample in Fig. 1, the acceptor densities and acceptor levels were determined by FCCS. The obtained values of N_{Al} , E_{Al} , N_{DA} , and E_{DA} were 1.6×10^{15} cm⁻³, $E_V + 0.24$ eV, 1.0×10^{15} cm⁻³, and $E_V + 0.41$ eV, respectively. Moreover, the compensating density (N_{comp}), which is the sum of the densities of donors and hole traps deeper than E_{DA} , was 2.6×10^{14} cm⁻³.

p(T) was numerically simulated using the following two equations:

$$p(T) + N_{\text{comp}} = N_{\text{AL}} f_{\text{FD}}(E_{\text{AL}}) + N_{\text{DA}} f_{\text{FD}}(E_{\text{DA}})$$
(4)
and

$$p(T) = N_{\rm V}(T) \exp\left[-\frac{E_{\rm F}(T) - E_{\rm V}}{kT}\right],\tag{5}$$



Fig. 1. Temperature dependence of hole concentration for Al-doped p-type 6H-SiC before and after irradiation with three difference Φ of 200 keV electrons. Since p(T) for the sample irradiated at Φ of 3 × 10¹⁶ cm⁻² could not be measured, the sample was annealed at 500 °C for 2 min. p(T) for the annealed sample was shown by +. The solid lines represent p(T) simulations with N_{Al} , E_{Al} , N_{DA} , E_{DA} , and N_{comp} obtained by FCCS.

where $E_F(T)$ is the Fermi level at *T*, $f_{FD}(E)$ is the Fermi–Dirac distribution function that is given by

$$f_{\rm FD}(E) = \frac{1}{1 + 4\exp\left[\frac{E - E_{\rm F}(T)}{kT}\right]},$$
 (6)

 $N_{\rm V}(T)$ is the effective density of states in the valence band, described as

$$N_{\rm V}(T) = 2 \left(\frac{2\pi m_{\rm h}^* kT}{h^2}\right)^{3/2},\tag{7}$$

 m_h^* is the hole effective mass and *h* is Planck's constant. Since the p(T) simulation (solid line) is in good agreement with the experimental data (\bigcirc) in Fig. 1, the values obtained by FCCS are reliable.

Using the other p(T) in Fig. 1, N_{AI} , E_{AI} , N_{DA} , E_{DA} , and N_{comp} were also determined by FCCS. Each p(T) simulation (solid line) is in good agreement with the corresponding experimental p(T).

Fig. 2 shows the dependence of N_{A1} and N_{DA} on Φ , denoted by \bigcirc and \triangle , respectively. With irradiation by 200 keV electrons at Φ of 1.0×10^{16} cm⁻², the decrement of N_{A1} is nearly equal to the increment of N_{DA} . At Φ of 3.0×10^{16} cm⁻², N_{A1} and N_{DA} in the 500 °C-annealed sample were shown by • and **A**, respectively.

Fig. 3 shows the dependence of N_{Al} , N_{DA} , and N_{comp} on Φ of 100 keV electrons, denoted by \bigcirc , \blacktriangle , and \Box , respectively. All the densities seemed unchanged by 100 keV electron irradiation. Therefore, 100 keV electrons could not displace any substitutional atoms in 6H-SiC, indicating that the threshold displacement energy (E_d) in 6H-SiC should be larger than 20 eV [12]. In this case, 200 keV electrons can displace only substitutional C (C_s), and neither substitutional Si (Si_s) nor Al_{Si} [12].

Two hundred keV electron irradiation creates V_C or interstitial C (C_i). One possible mechanism is as follows: One of the four C_s bonded to one Al_{Si} is displaced by 200 keV electron irradiation, and a complex (Al_{Si}–V_C) of Al_{Si} and V_C is created, indicating that N_{Al} decreases. By analogy with a B_{Si}–V_C complex in B-doped SiC [13,14], the deep acceptor in Al-doped SiC may be the Al_{Si}–V_C is displaced by the irradiation. This model leads to Eqs. (1) and (2).

One of other mechanisms is as follows: C atoms that are given energies by the irradiation migrate and react with Al_{Si}, and



Fig. 2. Dependence of N_{A1} and N_{DA} on Φ of 200 keV electrons. Since N_{A1} and N_{DA} in the sample irradiated at Φ of 3×10^{16} cm⁻² could not be obtained, the sample was annealed at 500 °C for 2 min. N_{A1} and N_{DA} in the annealed sample are denoted by • and \blacktriangle , respectively. The dependence of N_{A1} and N_{DA} on Φ , simulated using Eqs. (1) and (2) with κ_{A1} of 1×10^{-16} cm² and κ_{DA} of 9×10^{-18} cm², are shown by solid and broken lines, respectively.



Fig. 3. Dependence of N_{Al} and N_{DA} on Φ of 100 keV electrons.

complexes $(Al_{Si}-C_i)$ are formed, indicating that N_{AI} decreases. Moreover, other C atoms activated by the irradiation migrate and react with $Al_{Si}-C_i$, suggesting that N_{DA} decreases. This model also leads to Eqs. (1) and (2).

Although N_{Al} and N_{DA} in the sample irradiated with Φ of $3 \times 10^{16} \text{ cm}^{-2}$ could not be determined, they are expected to be 4.3×10^{13} and $2.1 \times 10^{15} \text{ cm}^{-3}$, respectively, by simulation using Eqs. (1) and (2) with κ_{Al} of $1 \times 10^{-16} \text{ cm}^2$ and κ_{DA} of $9 \times 10^{-18} \text{ cm}^2$. The simulations of the dependence of N_{Al} and N_{DA} on Φ represent the solid and broken lines in Fig. 2,

respectively. After annealing the sample at 500 °C for 2 min, N_{AI} and N_{DA} could be determined to be 4.0×10^{14} and 1.5×10^{15} cm⁻³, respectively. By annealing at 500 °C, N_{AI} is considered to be increased, and N_{DA} is decreased. From Fig. 2, furthermore, the increment of N_{AI} is expected to be nearly equal to the decrement of N_{DA} . This suggests that the 500 °C annealing transforms the deep acceptors into the Al acceptors.

According to literature [15–17], almost all defects were annealed out at higher than 750 °C. Only a few defects were annealed out at 400 °C, and were reported to be related to C_i [16]. Compared to V_c, C_i is rather mobile but can migrate and react with other defects or impurities [18]. By annealing at 500 °C, the following processes possibly occur in order to recover N_{A1} and to reduce N_{DA} : C_i migrates and reacts with Al_{Si}–V_c, or Al_{Si}–C_i releases C_i. Further research is in progress.

4. Conclusion

The changes of p(T) in Al-doped p-type 6H-SiC by irradiation with 100 or 200 keV electrons were investigated. Since p(T) was unchanged by irradiation with 100 keV electrons, 100 keV electrons could not displace any substitutional atoms in 6H-SiC. This indicated that E_d in SiC was higher than 20 eV, which meant that 200 keV electrons could not displace Al_{Si} and Si_s in Al-doped SiC. Therefore, 200 keV electrons could displace only C_s. By C_s displacement in Al-doped 6H-SiC, N_{Al} decreased monotonously with Φ , while N_{DA} initially increased and then decreased. By irradiation with 200 keV electrons with Φ of 1×10^{16} cm⁻², especially, the decrement of N_{Al} was nearly equal to the increment of N_{DA} . By annealing at 500 °C at 2 min, moreover, the increment of N_{Al} was close to the decrement of N_{DA} .

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